Renewable and Sustainable Energy Reviews 15 (2011) 366–378

Contents lists available at ScienceDirect

Renewable and Sustainable Energy Reviews

journal homepage: www.elsevier.com/locate/rser

Thermochemical conversion of biomass to second generation biofuels through integrated process design—A review

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ARTICLE INFO

Article history:
Received 21 July 2010
Accepted 21 July 2010

Keywords:
Biomass
Second generation biofuels
Process integration
Process design
Modelling
Optimization

ABSTRACT

The need for clean and environmental friendly fuels is leading the world to the production of biofuels and replacing conventional fuels by them. Second generation biofuels derived from lignocellulosic feedstocks tackle the drawbacks posed by the so-called first generation ones regarding feedstock availability and competition with the food industries. Thermochemical conversion of biomass to biofuels is a promising alternative route relying on well-established technologies including gasification and the Fischer–Tropsch synthesis. The conjunction of these processes creates a pathway through which the production of biofuels is sustainable. However, the multiple interactions between the processing steps greatly increase the difficulty in the accurate design of such processes. Detailed process modelling and optimization studies combined with process integration methods are necessary to demonstrate an effective way for the exploitation of these interactions. The aim of this work is to present and analyze the thermochemical conversion of biomass to second generation liquid biofuels as well as to indicate the emerging challenges and opportunities of the application of process integration on such processes towards innovative and sustainable solutions concerning climate concerns and energy security.

Contents

1. Introduction

Recent fluctuations in the oil prices and the growing concerns of a petroleum deprived future are driving the fuel market towards innovative and sustainable solutions. Biofuels have emerged as an

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doi:10.1016/j.rser.2010.08.003

alternative idea of escaping the currently predominant use of fossil fuels and petroleum for the production of power, heat and transportation fuels. The shifting of the global dependence on fossil fuels to renewable energy production technologies aims to the establishment of favorable environmental conditions and a sustainable economy [1]. The commitment of European countries to the Kyoto Protocol made also the development of biofuels a necessity in order to achieve the indented targets for energy policies and emissions reduction. The production of biofuels was mainly stimulated by the promise of low cost energy production when similar cost raw materials were used, the need to stimulate the agricultural sector, the desire for greenhouse gas (GHG) emissions reduction and the vast global availability and biodiversity of biomass [2]. Climate concerns and energy security, being the two main driving forces behind the development of the biofuel industry have boosted the production of biofuels in the EU over the past two decades as can be seen in Fig. 1.

Currently, the production of biofuels is limited to the so-called first generation biofuels comprising of biodiesel from vegetable oils and bioethanol from sugar containing plants. The production of first generation biofuels relies on well-established technologies and the actual exploitation of the final products is excellent. However, these biofuels exhibit significant costs mainly due to the limited feedstock species that they account for. Furthermore, a competition was developed between the biofuel and the food industries over the subject of feedstock availability and other potential – mainly economical – imbalance that the use of these materials for fuel production would have on the food industry and society in general. Great consideration is also taken about the use of land, water and chemical fertilizers that the cultivation of these plantations requires, both in environmental and economic levels.

On the other hand, second generation biofuels derived from lignocellulosic feedstocks overcome the problem of feedstock availability enabling the use of a much broader variety of biomass sources. Second generation biofuels originate from agricultural residues and by-products, organic wastes and materials derived from purposely grown energy plantations [4], offering a more preferable variety of woody, grassy and waste materials as a feedstock. The flexibility in these types of resources tackles the competition between the food companies and further ensures the sustainable development of biofuels. Although second generation biofuels are still under technological investigation regarding conversion technologies and process operation, they are expected to meet requirements for lower land use and much better CO_2 emissions reduction potential after commercialization [5]. Second generation biofuels are compatible with today's fuels and the necessary infrastructure may come, to some extent, from the existing infrastructure of the petroleum and sugar industries. It is believed that the market transition from first to second generation biofuels will be slow but steady, with a basis on this compatible infrastructure. Second generation biofuels are expected to be slowly integrated in the first generation biofuels market and after commercialization through strenuous technological investigation, finally become the predominant fuel products [4]. Of course, the economic feasibility and success of these biofuels strongly depends on the legislation and taxation policies invoked upon their introduction in the energy market. Thus, such favorable policies on country and national levels are mandatory for the successful introduction and distribution of these biofuels into the market.

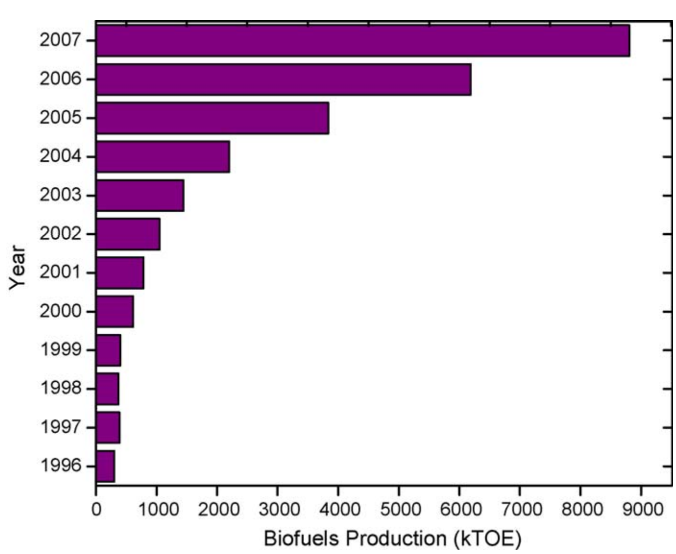


Fig. 1. Biofuels production in the EU over the past years [3].

Second generation biofuels are mainly produced through two distinct conversion routes, namely the thermochemical and the biochemical one, each having its own technological pathways, benefits and drawbacks. The thermochemical route consists of the pyrolysis and/or gasification and subsequent gas cleaning and conditioning processes, followed by the Fischer–Tropsch (F–T) synthesis for the production of synthetic liquid fuels. The biochemical route involves the enzymatic transformation of cellulose and hemi-cellulose to sugars and subsequent fermentation to bioethanol. This route, although having more cost reduction potential due to its most recent development and constant effort for optimization, is less prone to commercialization than its alternative, which employs processes that have been thoroughly studied through the years [4]. Although the two production routes mentioned above are the most common, they are not the only existing pathways in the biofuel industry as there are other alternatives currently being tested in laboratory and pilot plants [4]. Huber et al. [6] provide an excellent review of the possible biomass conversion strategies for the production of second generation biofuels. The main biofuel production pathways are depicted in Fig. 2.

Biomass gasification and subsequent catalytic Fischer–Tropsch's synthesis are key technologies for second generation automotive biofuels production. However, this promising combined process is still far from commercialization and only pilot plants are available at the time, most of them being situated in Europe as reported in Table 1.

The scarcity of these plants is due to the fact that this promising biomass-to-liquid fuel process is still under strenuous investigation for optimization. However, the combination of the processes that constitute the thermochemical biomass conversion route along with the different choices for systems and operating parameters make the development of an economic and viable system a rather difficult and demanding task. For example, the choices of the type of gasifier or the operating conditions prevailing determine the CO_2 emission profile that, in turn, is also determined by the type of raw material (i.e. its classification as a waste product or an energy crop). These choices also directly affect the overall investment and operating costs, a parameter with utmost importance when discussing about new and developing technologies. Nevertheless, in order to exploit the maximum efficiency of such a process, all the potential interactions between the various processing steps and also the flexibility that the process must have should be taken into consideration. The above are determined by the variability of demand, prices and feedstock availability. A target like that can only be achieved through the rigorous optimization of an integrated biomass conversion scheme.

Although some international studies and reviews deal with biomass and the production of second generation biofuels through thermochemical conversion processes [4,8,9,10,11,12], sometimes extending towards the co-production of energy

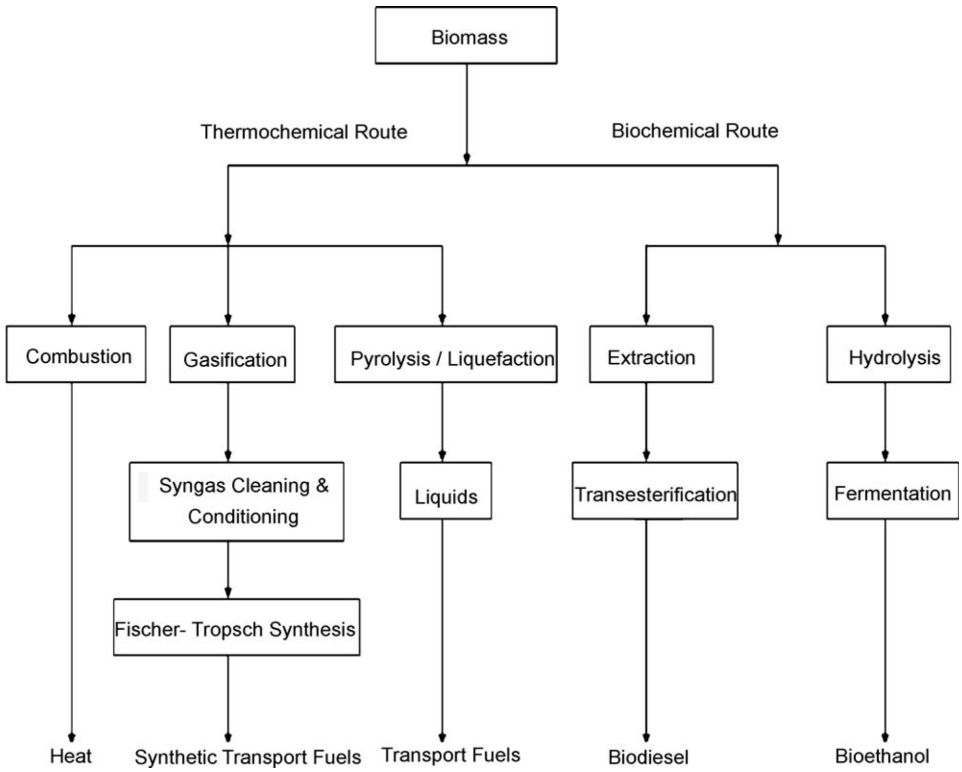


Fig. 2. Simplified schematic illustration of the two main biofuel production pathways.

Table 1
Second generation biofuel plants worldwide [7].

Company/Institute Name	Location	Type	Start-up	Output
Vienna Univ. of Technology	Gussing (Austria)	Pilot	2005	0.02 t/y
Forschungszentrum Karlsruhe GmbH	Karlsruhe (Germany)	Pilot	U/C[a]	608 t/y
CHOREN Tech. GmbH	Freiberg (Germany)	Pilot	2003	100 l/day
Cutec	Clausthal-Zellerfeld (Germany)	Pilot	1990	0.02 t/y
CHOREN Tech.GmbH	Schwedt (Germany)	Com.[b]	2010	200,000 t/y
ECN	Petten (Netherlands)	Pilot	2011	346 t/y
ECN	Alkmaar (Netherlands)	Demo	Planned	28,800 t/y
NSE Biofuels, NESTE Oil and Stora Enso JV	Vakaus (Finland)	Demo	2009	656 t/y
Research Triangle Institute	N. Carolina (USA)	Pilot	Planned	22 t/y
GTI Gas Technology Institute	Illinois (USA)	Pilot	2009	26 t/y
Flambeau River Biofuels LLC	Wisconsin (USA)	Pilot	2011	51,000 t/y

[a] U/C, under construction.
[b] Com., commercial.

through gasification combined cycles [13,14,15,16] or employing fuel cell technology [17,18,19], few address the issue of integrated thermochemical conversion systems for the production of liquid biofuels. This work aims to stimulate this need for an integrated approach for the production of second generation biofuels via the thermochemical route. The main processing steps for the conversion technology are presented and process modeling studies and optimization approaches which are mandatory for the determination of the optimal operating range of each processing step are investigated. Lastly, integration possibilities for the investigation and exploitation of potential interactions between these steps are explored and presented.

2. Processes of thermochemical conversion of biomass

2.1. Gasification

Gasification is the thermochemical transformation of a raw material into a gaseous mixture through a series of chemical reactions listed in Table 2 with a controlled amount of air and high temperatures. The gaseous product is an energy rich mixture of H_2, CO, CO_2, CH_4, C_2H_4 and other impurities such as nitrogen, sulfur, alkali compounds and tars. Gasification is possible by using oxygen, air, steam or mixtures of these as the gasifying agent. Air gasification results to a product with low to medium heating value 4–7 MJ/N m), while gasification with oxygen or steam leads to a product with medium heating value (10–14 MJ/N m). When steam is used, more hydrogen is produced from the reaction of methane

Table 2
Basic gasification reactions [18].

Reaction	ΔH (kJ/mol)
$2C + O_2 \leftrightarrow 2CO$	+246.4
$C + O_2 \leftrightarrow CO_2$	+408.8
$CH_4 + H_2O \leftrightarrow CO + 3H_2$	−206
$CH_4 + 2H_2O \leftrightarrow CO_2 + 4H_2$	−165
$C + CO_2 \leftrightarrow 2CO$	−172
$C + H_2O \leftrightarrow CO + H_2$	−131

reforming which leads to a product stream with higher hating value [20]. However, gasification with steam requires higher operating temperatures for the vaporization of water making it a more expensive alternative. Therefore, the use of a mixture of air/steam with a variable inlet ratio is useful in order to better exploit the benefits of each fluidizing gas.

Gasification reactors usually operate at high temperatures (800–900 °C or even higher) and regardless of their type and configuration, their operation consists of four steps namely drying, pyrolysis/devolatilization, reduction and combustion. In the drying section of a gasifier, the feedstock is stripped of its moisture content (usually high for biomass feedstocks). In the pyrolysis zone, volatiles are removed in the form of light hydrocarbons, CO and CO_2 and also liquid long-chain hydrocarbons known as tar are produced. The formation and nature of the produced tar largely depends on the type of feedstock as well as the operating conditions and gasifying agent [21]. The reduction zone serves as the main process where the raw materials are completely gasified using oxygen from the air and/or steam in order to form the syngas product through a series of endothermic reactions. Lastly, in the combustion section, the residual char matrix is further burned producing more gaseous products and the necessary heat for the reactions in the reduction zone.

For the purpose of handling different kinds of raw materials, especially when considering the different nature of globally available biomass feedstocks, various types of gasification reactors were developed which can primarily be classified into three main categories; fluidized bed, fixed bed and entrained flow reactors. Large scale (industrial) applications usually employ entrained flow or fluidized bed gasifiers, while fixed bed gasifiers are preferred for small scale gasification.

The operation of fluidized bed gasifiers is based on the fluidization of a bed of grainy porous material offering the advantage of a uniform temperature distribution and better solid–gas contact and heat transfer rates [21]. These gasifiers are equipped with cyclone separators in the top section for the removal of the particulates from the product stream. Depending on the fluidization pattern, such gasifiers can be further sub-classified into bubbling and circulating fluidized bed gasifiers. In the first, the fluidization gas passes through the bed creating a bubbling section where the reactions take place. The gas is injected into the reactor from the bottom through a gas distributor. Optimal design of these systems can lead to controlled bubble coalescence in fluidized bed reactors and as such, in improved gas–solid heat transfer rates [22]. Bartels et al. [23] address the problem of particle agglomeration within a fluidized bed giving a comprehensive review and suggestions for countering this phenomenon. In most cases where silica sand is used as the bed material, the silica particles can potentially form low boiling point silicates with the inorganic portion of biomass. These silicates, when melt due to the high operating temperatures, form an adhesive layer that binds the biomass particles forming agglomerates and ultimately stopping fluidization. In the circulating fluidized bed gasifier which is a natural extension of the bubbling bed gasifier, the bed is circulated between the reaction zone and the cyclone separator which captures the solids content of the product gas and recycles it into the reactor prolonging its residence time. Li et al. [24] present a study of a pilot scale circulating fluidized bed gasifier, examining various operating parameters and comparing the results with a free Gibbs energy minimization model.

In fixed bed gasifiers, the gas passes through the raw material while the gasifier zones are in "fixed" position and the reactions take place. The biomass enters the vessel from the top section and depending on the flow of the gasifying agent these gasifiers can be further classified as updraft or downdraft. Cross-flow gasifiers have also been developed where the gas enters the gasifier from a side section and the gases are collected from the opposite side. Due to the different mixing and flow conditions in each of these configurations, the final product may be greatly different in terms of temperature and composition, tar and particulates content and thermal efficiency. The advantages and disadvantages of these types of fixed bed gasifiers are summarized by McKendry [21], while Warnecke [25] gives an excellent and detailed comparison of fixed bed and fluidized bed gasifiers presenting the differences of these two reactor types in both technical and operating parameters.

Entrained flow reactors usually operate in higher temperatures (1200–1600 °C) and pressures (2–8 MPa) and require a rather uniform particle size distribution for the feedstock [26]. However, as this can be problematic with the fibrous nature of most biomass feedstocks, this gasifier type is mostly preferred for the gasification of coal. Another drawback of entrained flow gasifiers is that due to the high operating temperatures, the ash contained in most biomass feedstocks reaches its melting point and becomes a slag that is sometimes, depending on the origin of the feedstock, corrosive. Entrained flow gasifiers exhibit high capacities and enable large throughputs with low tar content in the final product mainly due to the elevated operating temperatures and short residence times [27]. The characteristics of the most common gasification reactor types used in the biomass industry up to date are presented in Table 3.

The production of tars from the pyrolysis section in a gasifier is generally undesired when the main purpose of the process is the production of syngas for synthetic fuel production or electricity generation. Due to their viscous nature and the fact that they tend to condense in low temperatures, they are sometimes responsible for operating failures such as equipment blocking and fouling. The production of tar is mainly affected by the type of the gasifier used. For example, it is known that fixed bed downdraft gasifiers tend to give the least amounts of tar [21]. The reduction of the tar content in the gasifier is performed through careful design of the process via the optimal selection of the operating parameters, use of proper catalysts for the inhibition of tar formation and process modification. Cleaning of the syngas product is also possible using mechanical (cyclones, filters) or chemical (tar cracking) methods [28]. These methods for tar reduction or elimination are presented in detail by Han and Kim [29].

The ash remaining in the gasifier can be removed as dry ash or as slag in cases where the operating temperature exceeds the ash fusion temperature. The formed slag sometimes acts as a corrosive agent depending on the nature of the feedstock and needs to be removed for the protection of the gasifier internals. Dry ash gasifiers are equipped with ash collection grates where the ash is collected and removed. In the case of fluidized bed gasifiers,

Table 3
Main characteristics of the common industrial gasifiers.

Gasifier type	Characteristics
Fixed bed	Can handle large and coarse particles Release lower temperature gas product High particulate content in gas product stream High gasifying agent consumption Ash is removed as slag or dry
Fluidized bed	Uniform temperature distribution Better gas–solid contact High operating temperature (1000–1200 °C) Low particulate content in the gas stream Suitable for feedstocks with low ash fusion temperature Ash is removed as slag or dry
Entrained flow	Need finely divided feed material (<0.1–0.4 mm) Very high operating temperatures (>1200 °C) Not suitable for high ash content feedstocks Very high oxygen demand Ash is removed as slag Short residence time

cyclone separators are also useful for the capture and removal of the ash from the gaseous product.

2.2. Syngas processing

The syngas from the gasification reactor can be used in a number of ways, including direct use in internal or external combustion engines for electricity generation in the range of 0.1–10 MW_{el} [30], liquid biofuel synthesis or solid oxide fuel cell (SOFC) application. Depending on the application of the product syngas, various quality restrictions have to be considered for the operation of the gasifier. For example, application of the product in SOFC requires high hydrogen content for the gas to be efficiently used in such a process [18], while the other two require hydrogen to carbon monoxide (H_2/CO) ratios dependent on the subsequent process. Regardless of the application of the syngas, the gaseous product needs to undergo a cleaning and purification step. The hot syngas from the gasifier unit is a high temperature gaseous mixture containing impurities in the form of solid particles, alkali and sulfur compounds and condensable tars. The syngas cleaning is possible in three temperature ranges, characterized as cold, warm and hot cleaning for temperatures below 30 °C, 30–300 °C and above 300 °C respectively. The cleaning temperature depends on the choice of technology as well as the intended use of the produced syngas.

Gas cleaning from the impurities is an essential step as the particulates may cause damage to the transportation equipment and the tars could be responsible for equipment fouling. Especially in the case of Fischer–Tropsch's synthesis for the production of synthetic liquid biofuels, the syngas must also be rid of its sulfur content to avoid catalyst poisoning. Gas cleaning is achieved with the help of filters for the capture of the particulates while sorbents are used to remove the alkali and sulfur compounds that pass on from the raw biomass to the gasification effluent gas. Finally, the chemical destruction of tar is achieved through catalytic steam reforming or thermal cracking methods.

2.2.1. Particulates and impurities in syngas

Usually ceramic or metal-based filters are used for the removal of the particulates from the product syngas. Sharma et al. [31] explain the difficulties and challenges that these filters meet in terms of performance as many factors such as the filter material (metallic, ceramic, etc.) and design of both the filter and the filtration unit with regard to the syngas conditions and composition must be taken into consideration. Also, clogging due to ash deposition on the filter surface is an important factor that may hinder the process. The same authors report the development of novel technologies for the removal of the particulates, including particle agglomerating methods and integrated gasification–gas cleaning processes. High porosity nanoparticle membrane filters are also in development for the capture of sticky material that can be formed during the gasification step depending on the process operating conditions [32].

The stripping of the syngas from the inorganic compounds is mostly performed in fixed bed vessels where the syngas passes through the sorbent bed and is stripped of its alkali and sulfur content. According to Sharma et al. [33], in order for a sorbent to be efficient for the removal of alkali and sulfur compounds, it must have a very high sorption capacity with high resistance to particle attrition and sintering due to the high operating temperatures. The sorption capacity is a direct function of the material's porosity, meaning that the more void the material matrix is, the more capacity it has for the cleaning process. However, a large porosity means low tensile strength of the material so a compromise has to be made between the two in order for the best solution to be found.

Due to the importance of the syngas conditions and composition in a chemical industry, the cleaning and impurities removal is an essential step that receives continuous attention. The design of processes for the removal of impurities with the help of sorbents as well as filter design is areas with utmost importance and the constant need for improving their reliability and efficiency strongly reflects their importance for the viability and commercial success of the biomass conversion process.

2.2.2. Tar removal

During the pyrolysis and subsequent gasification of biomass, the interconnections between its three basic constituents (lignin, cellulose and hemi-cellulose) collapse due to the high reaction temperatures and the chemical bond breaking results in the transformation of the solid material into a liquid one. This liquid material, known as tar is a mixture of diverse ring structure hydrocarbons. Tar can be immediately evaporated into syngas upon formation by using high temperatures, while slow temperatures result in its condensation to a residual char matter [34]. Due to its condensable character, tar poses a threat to process equipment, as it can block or inhibit the operation of turbines and engines by increasing attrition as well as by causing fouling, clogging and in general, it decreases the overall gasification efficiency. As mentioned above, the formation of tar in the gasifier can be controlled through the process operating conditions, the type of the gasifier and the use of proper additives/catalysts for tar formation inhibition [28]. If good care is taken during the gasification step a very clean syngas can be produced. Secondary tar removal processes include physical methods such as gas filtering using various filter types, gas scrubbing and cyclone separators, or chemical methods such as catalytic steam reforming and thermal cracking for hydrogen production. However, some of these physical processes, such as the gas scrubbing, are deemed economically unpractical when working on elevated temperatures and as such, they are not preferred for hot cleaning applications [35].

Steam reforming is one of the most common methods of commercial bulk hydrogen production and involves the reaction of the product tars with steam at temperatures around 650–700 °C, through which hydrogen is mainly produced. The hydrocarbons contained in the tar react with steam via the irreversible reaction [36]

$$C_xH_y + xH_2O \rightarrow xCO + (x + y/2)H_2$$

while additional hydrogen is produced through the water gas shift reaction

$$CO + H_2O \leftrightarrow CO_2 + H_2$$

During steam reforming, the formation and deposition of coke in the reactor is possible. This is an unwanted side product that can cause fouling of the process. Coke formation is suppressed by steam which favors the reforming reactions. Therefore, a sufficient amount of steam has to be fed into the reactor. Steam reforming can be conducted in a single step inside the gasifier or as a second step, in a separate reaction vessel after the gasification. It is evident that the first case is preferred as there are numerous advantages including the simultaneous production and improvement of the syngas composition and the increased hydrogen yields. Also, the minimization of piping and equipment results in reduced capital costs and the reduction of the process susceptibility to the condensed tar. However, single step tar removal is a very difficult and demanding task and usually a reforming process is used in the gasifier for product upgrading, while a second tar removal process follows. Depending on the reaction conditions which specify the final product distribution, the final syngas H_2/CO ratio is determined. This ratio, in turn, can be a decisive parameter for the kind of application of the produced syngas. The reverse also applies as the reforming process can be designed in order to

produce syngas with a desirable H_2/CO ratio depending on the intended use.

Steam reforming can take place in conventional fixed bed [37,38], fluidized bed [37] or in novel membrane reactors [39]. Commercial catalysts used for tar reforming include metal-based catalysts or combinations of metals with carbonaceous or silicate minerals [37,40]. Nickel is a cheap alternative between the metal and alkali metal catalysts available and exhibits very good tar removal properties. Cobalt catalysts are also reported as useful catalysts for steam reforming [36].

Tar cracking includes the thermal cracking of the long hydrocarbon chains that constitute tar into smaller molecules. Tar cracking methods result in the production of CO and H_2 as well, enriching the final gaseous product. Similar with steam reforming, tar cracking can be performed in the gasification reactor or in a separate vessel. Usually, various minerals and metal oxides are used as catalysts for promoting tar cracking. Dolomite and olivine have been proposed as suitable bed materials for fluidized bed gasifiers that lead to the thermal cracking of tar [35,41]. Although dolomite has been known for its tar cracking promoting capabilities for a longer period of time, it was reported that olivine exhibits the same efficiency only with better attrition resistance properties [42]. These natural minerals are cheap but fail to reach the low tar criteria that the syngas needs for further use in Fischer–Tropsch's synthesis. Nickel based catalysts on the other side provide almost complete tar destruction, but they are easily deactivated by char disposition. To counter that, some technologies use two distinct tar removal units, one being the gasifier itself, where minerals are used for the first step of tar cracking and the second being another catalytic steam reforming reactor equipped with nickel-based catalysts for the complete removal of tar [43].

In a novel syngas processing method, Leibold et al. [32] propose a combined syngas cleaning scheme for subsequent Fischer–Tropsch's synthesis where the sorption stage together with a catalytic tar reforming process is combined with the particulates filter in order to efficiently rid the syngas of all impurities. According to their proposal, the sorbent is dispersed in the form of powder on the filter, while a catalytic surface is placed on the clean side of the filter. In this way, the sulfur and alkali compounds are removed first, followed by the particulates and the tar. The process could be operated at elevated temperatures and placed directly after the gasification step, with the temperature being adjusted to the synthesis temperature at the end of the cleaning process.

2.3. Fischer–Tropsch's synthesis

Fischer–Tropsch's (F–T) synthesis is a process developed by Franz Fischer and Hans Tropsch in the 1920s that includes a set of chemical reactions through which a mixture of hydrogen and carbon monoxide (syngas) is converted into long chain liquid hydrocarbons. The product is a synthetic petroleum substitute that can be used as fuel oil in the automotive industry. The F–T chemical transformation process is expressed through the following set of reactions:

$$(2n+1)H_2 + nCO \rightarrow C_nH_{(2n+2)} + nH_2O$$

where n is a positive integer representing the length of the hydrocarbon chain. The process is usually operated in a temperature range of 150–300 °C and at an elevated pressure of some tens of atmospheres, both of which inhibit the formation of short chain hydrocarbons, such as methane. Long hydrocarbon formation and high product yields are obtained at these conditions but the costly high-pressure equipment that is needed for the conversion must be considered in the design of the process.

The chemical conversion of syngas into hydrocarbons is mostly catalyzed by transition metal-based catalysts, the most common of which being cobalt and iron. Cobalt catalysts reach their optimal operation at high H_2:CO ratios (close to 2), while iron-based catalysts can handle a syngas feed with a lower H_2:CO ratio due to their inherent ability to promote the water-gas shift reaction, through which more hydrogen is produced. The design of catalysts for the Fischer–Tropsch synthesis is an area receiving much attention [44–47] as their performance strongly influences the distribution of the final products. All Fischer–Tropsch's catalysts are well-known for their sensitivity to sulfur and thus, a carefully designed desulfurization step prior to the insertion into the Fischer–Tropsch reactor is deemed necessary in order to avoid catalyst poisoning.

The synthesis of long chain hydrocarbons through the Fischer–Tropsch reaction can be considered analogous to a polymerization reaction. The product distribution of the reaction is expected to follow the exponential Anderson–Schulz–Flory (ASF) distribution which describes the successive addition of carbon atoms into the molecule chain and is expressed through the following equation [48]:

$$\frac{W_n}{n} = (1-a)^2 a^{n-1}$$

where W is the weight fraction of the molecules that contain n carbon atoms and α is a parameter that strongly depends on the process operating conditions and catalyst type and represents the chain growth probability. Large values of this parameter signify a high probability for long chain products while the opposite is expected from small values.

Fischer–Tropsch's synthesis takes place in conventional fixed bed, fluidized bed or slurry bubble column reactors. Fischer–Tropsch's reactors can be classified according to the number of phases they account for. Fixed bed, fluidized bed and circulating fluidized bed reactors employ two phases (gas–solid) while the slurry bubble reactor contains the liquid phase in direct contact with the solid catalyst and the gas bubbles flowing upwards through the liquid phase. Bubble column reactors exhibit the best efficiency due to the increased mass transfer rates but as the separation of the catalyst from the products is difficult, alternative reactor configurations are sought.

Guettel and Turek [49] present a comparison between conventional reactors and novel micro- and monolithic reactors based on simulation results. The authors conclude that although monolithic reactors offer the same results in terms of productivity with the fluidized bed reactors, they pose a challenge in commercialization as there is a large need for catalyst recycling. Micro-reactors appear to be the best choice for Fischer–Tropsch's synthesis if the ratio of catalyst to reactor volume is significantly increased. Davis [50] gives an analytic review of the progress in Fischer–Tropsch's reactor development from the time of the process' discovery up to the last decade.

The final product distribution of a Fischer–Tropsch's synthesis process strongly depends on various operating parameters. Kim et al. [51] present a study including the impact of the process operating temperature on the results of the Fischer–Tropsch synthesis carried out in slurry bubbling bed reactor with the presence of a Co catalyst, while Wang et al. [52] devised a model for the prediction of the behavior of a fixed bed reactor. Their results also show the effects of operating and structural parameters of the process such as the tube diameter, the recycle ratio, pressure and temperature on the product yields. A model for the prediction of the behavior of a slurry bubble bed reactor is presented by Fernandes [53] in an attempt to find an optimal solution for the process operating parameters with respect to the maximization of the products. Tian et al. [54] studied the effect of the reaction conditions on the activity and selectivity of an iron catalyst and the subsequent results on the product distribution

using Monte-Carlo simulations. They have concluded that the reaction temperature is a major factor that can directly influence the latter. Lastly, in reactors with structured packings the operating temperature can be indirectly controlled by improving the heat transfer characteristics. Pangarkar et al. [55] evaluated the performance of four types of structured packing for heat removal and their application as a catalyst support for Fischer–Tropsch's synthesis.

2.4. Fischer–Tropsch's wax hydrocracking

Naturally, Fischer–Tropsch's synthesis produces a distribution of linear paraffins and olefins with a wide range of molecular weights through the ASF correlation. The chain length of these hydrocarbons can vary according to the operating conditions and catalyst properties and as such, it is possible that long chain heavy paraffins, which constitute a waxy material, will be produced. Under the operating conditions of a typical Fischer–Tropsch's synthesis process these waxes with a boiling point of over 370 °C will be in the liquid state [56] and can be further cracked down to medium molecular weight hydrocarbons that include gasoline, kerosene and other liquid fuels. Thus, cracking of the Fischer–Tropsch waxes can significantly enhance the final products quality as the synthetic fuels produced are upgraded due to the extra products from the hydrocracking step.

Wax cracking involves the processing with hydrogen for the chemical fragmentation of the long chain hydrocarbons into hydrocarbons of desired chain length. The mechanism of molecule breaking involves the continuous transformation of the initial linear molecule into multi-branched isomers and the subsequent cracking of the branches to lighter products [57]. It is also reported that the internally located carbon bonds in a hydrocarbon chain are more susceptible to chemical cleavage while the endpoint carbon bonds exhibit less scission reactivity [58].

Hydrocracking is mostly carried out in fixed bed tubular reactors with the utilization of bifunctional catalysts which include both acidic sites acting as promoters of cracking and isomerization and metallic sites that promote hydrogenation and dehydrogenation [59]. Commonly used catalysts include Pt, Pd or bimetallic systems like Ni/Mo, Ni/W, Co/Mo in their sulphided forms supported unto substrates such as oxide mixtures, zeolites or silicoaluminophosphates. The degrees of isomerization and hydrocracking can be modulated through the careful selection of the catalyst system [60]. Ideally, the process should be designed in a way that promotes the breaking of the chains until a certain point that constitutes a design parameter is reached. The latter need is often implemented into the catalyst design for the hydrocracking process as the nature and the properties of the selected catalyst can be used for controlling the molecular weight range of the products.

3. Process integration for the production of second generation biofuels

3.1. Process integration

Process integration refers to a holistic approach that takes into account all the possible interactions between the various steps of a process and the exploitation of these interactions in order to achieve the minimization of the overall investment cost, higher product yields and an efficient process design. This approach is advantageous to the design of a process as it considers the optimization of the system as a whole while the opposite would result in an attempt to present the system as a combination of distinct processes. The latter means that all the potential beneficial interactions between these processes would be neglected. Process integration can be used as a tool in process design studies both for the design of new processes and plants and in retrofit designing of old processes (optimization of an existing process).

Integration is possible by means of heat exploitation and the combination of the energy streams of a process in order to utilize high temperature streams to provide heat to another part of the same process. In this way, an autonomous operation is achieved as less external heat supply is needed. Moreover, substantial economic benefits arise from this as the cost reduction due to the exploitation of the otherwise useless high temperature streams becomes significant. Heat integration was the main focus of the researchers in the late 1970s and 1980s which resulted in the development of various techniques such as pinch analysis and the design of heat exchanger networks [61].

Pinch analysis is an evaluation tool that emerged in the late 1970s which aims to minimize the energy consumption of a process by setting thermodynamic targets, as well as the course to achieve them, through an optimization of heat supply pathways and process operating conditions [62]. With pinch analysis the process heat flow streams are combined into groups of hot and cold streams and composite curves are formed. These curves represent the set of hot and cold streams (streams releasing or requiring heat respectively). The point of closest approach between these curves is the pinch temperature, the best point to start the design studies. Heat exploitation is possible with the use of heat exchangers between these streams in groups, the selection of which is part of the design problem.

A typical example of heat integration and co-production of electrical energy and products from biomass/coal gasification is the integrated gasification combined cycle (IGCC). In the IGCC a gasification unit is coupled with gas and steam turbines for the production of electrical energy. Usually coal is fed as the raw material in the gasifier where the gasification reactions take place in high temperature and pressure. Various options are available for the type of the gasifier used and like conventional gasification processes, each has its advantages and drawbacks. The product stream consisting of a mixture of gases as well as unreacted coal and ash is cooled by a gas scrubber and the excess heat is used for the production of high pressure steam (HPS). Separation processes are needed to remove the sulfur content as well as the carbon and ash fragments and part of the clean syngas is fed into a gas turbine. The heat from the gas turbine is then used to produce additional steam which is led through a steam turbine in order to produce electrical power. An illustration of an IGCC presenting all the intermediate processing steps described above can be seen in Fig. 3.

More recently, pinch analysis has been extended to the field of mass integration, where the combination of material streams for the valorization of the process wastes occurs [61]. Mass integration involves the utilization of stream recovery, recycle and mixing to identify cost-effective conservation schemes. The need of modern industries for waste management and reduction has led to the development of systematic methodologies for the utilization of waste streams. The more stringent environmental protection regulations have driven the design of new processes and the reconstruction of old ones with respect to financial competitiveness towards new directions, where simultaneous heat and mass integration methodologies along with process optimization tools for the determination of the optimal process configuration and operating conditions are essential for the viability of these processes.

Integration is also possible by means of process intensification, a trend consisting of the development of innovative techniques that provide drastic improvements in the field of chemical processing. These include the use of modern process configurations that aim to the decrease of the equipment volume and energy consumption, the maximization of the production and the improvement of the process sustainability [63]. Typical examples

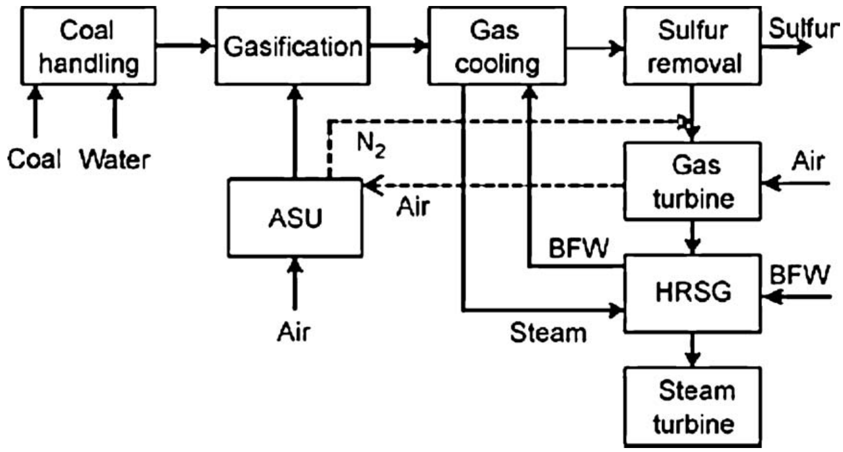


Fig. 3. Simplified flow diagram of an IGCC [14].

of process intensification are reactive or extractive separations in which chemical reactions (or extraction) along with physical separations occur simultaneously inside the same process unit. Another example that accounts for the thermochemical conversion of biomass is the design and implementation of a catalytic reforming step inside the gasification vessel for the upgrading of the produced syngas quality. The resulting intensified processes are able to yield high purity products with significantly lower investment cost compared to a system encompassing both processes separately. The latter stems from the implementation of the two units into one, which results in a hybrid process occupying less volume and yielding higher purity products. However, it is apparent that these intensified processes require more rigid design compared to the typical simple processes due to their complex nature.

3.2. Integration possibilities for the thermochemical conversion of biomass

In order for the full potential of a thermochemical biomass-to-liquid (BTL) process to be achieved, every interaction between the processing steps must be taken into account. This will result in a fully integrated process scheme that will consider both material and heat streams and provide a synergistic route through which the combined exploitation of these will be possible. A proposed integrated scheme for the production of second generation biofuels is presented in Fig. 4 where one can observe all the possible interactions between the processing steps.

The production route of second generation biofuels through the thermochemical conversion of biomass can be summarized in three main processes as described above, namely pyrolysis/gasification, syngas cleaning and conditioning and Fischer–Tropsch's synthesis. Each of these involves a number of operating parameters and decisions that must be taken into consideration for the process design. Typical examples are the type of the gasifier, the gasification medium, syngas cleaning equipment, Fischer–Tropsch's catalysts and much more. In order to achieve maximum efficiency for the process all these parameters need to be co-evaluated.

In general, the pyrolysis/gasification step provides three different product species. These are the gaseous products in the form of syngas, the liquid products in the form of the condensable tars that are mostly drifted in the syngas and lastly, the solid products which are comprised of the char residue. It is already mentioned that the tars produced in the pyrolysis zone of the gasifier are an unwanted side product when the production of synthetic fuels through Fischer–Tropsch's synthesis is sought. However, these tars can be further chemically processed in order to provide additional synthesis gas that can be used in two ways depending on its composition. Syngas with a H_2/CO ratio close to 2 can be additionally fed to the Fischer–Tropsch reactor after undergoing cleaning for impurities, while higher H_2/CO ratio would enable the use of the hydrogen-rich syngas for the hydrocracking of the Fischer–Tropsch waxes.

Tar processing can be achieved by means of catalytic steam reforming or thermal cracking as reported in Section 2.2. Possible

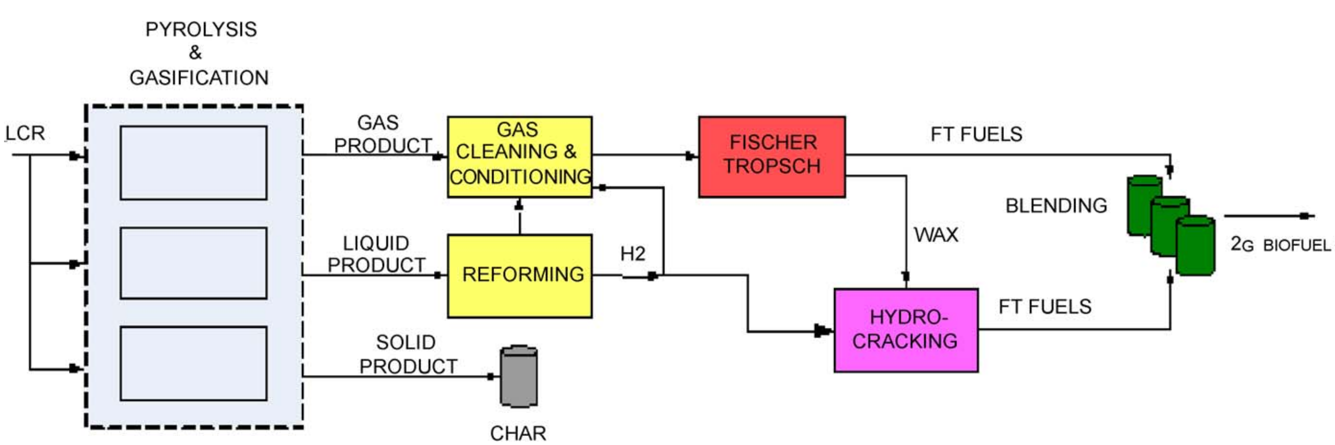


Fig. 4. Integrated biomass thermochemical conversion scheme for the production of second generation biofuels.

integration of tar processing methods inside the gasifier will improve the economic viability of the overall process as the combination of the two processes into one will help achieve an intensified and beneficial result in less operating volume. The choice of technology between these two tar destruction process alternatives strongly depends on the overall gasifier design. For example, gasification with steam makes the choice for an integrated catalytic steam reforming step for the preliminary tar removal a viable option. The composition of the produced syngas, in turn, will determine the need for a second tar removal step external to the gasifier. Process operating conditions for the syngas cleaning and conditioning step, both for the removal of the particulates and impurities and the possible secondary tar removal will once again be determined based on the syngas composition and the gasifier conditions.

A possible subsequent process in the production scheme will also play a part on the decisions for the operating parameters for this step. For instance, hot cleaning at temperatures close to these of the syngas exiting the gasifier would be convenient in order to minimize heat losses, but in the case of syngas use for Fischer–Tropsch's synthesis this has little meaning. In fact, as Fischer–Tropsch's synthesis reactors operate at lower temperatures (below 300 °C), hot cleaning has very little energy profits, especially when additional compression is required to reach the operating pressure for the Fischer–Tropsch reactor [64]. Syngas cooling and exploitation of the heat through heat integration methods is required to reduce thermal losses. Also, as the extent of the Fischer–Tropsch reactions strongly depends on the process conditions (feed flows, reactor sizing, etc.), care should be taken for possible unreacted H_2 and CO through carefully designed recycle streams.

The implementation of a Fischer–Tropsch's wax hydrocracking process into the thermochemical conversion scheme ensures the utilization of the high molecular weight fraction of the hydrocarbon mixture produced by the process. This fraction is processed with hydrogen and reduced to a mixture of medium molecular weight hydrocarbons which is blended with the actual Fischer–Tropsch's product. Blending of the Fischer–Tropsch products with the ones derived from the hydrocracking stage not only enriches the quality of the liquid biofuels but also offers a high efficiency integrated process. A part of the necessary hydrogen for the hydrocracking of the Fischer–Tropsch waxes can be obtained from the tar reforming step, if a high enough H_2/CO ratio syngas is produced through the reforming process. The latter is subject to the design of the reforming step, concerning both the operation conditions and the catalyst design that needs to account for high hydrogen production.

It is evident that the integration of various processes into a combined thermochemical conversion scheme sets a lot of speculations about the design strategy. The numerous interactions between these individual processes multiply the process complexity and the optimal design solution, although guaranteed to provide a more efficient and economically viable overall process, needs much more effort to be found. In order for this solution to be obtained, one must examine and evaluate all the possible operating scenarios before choosing the one that encompasses the best solution. The latter is possible through the use of modern process modeling tools and process integration methods.

4. Modeling approaches

Process modeling is a powerful tool which allows the mathematical representation of a process and the comprehensive study of its features and structure. By using an accurate and robust model, the qualitative examination and analysis of various options regarding the system's operating conditions in order to determine the optimal range of performance becomes possible. Moreover, process modeling enables the quantitative evaluation of various process alternatives such as different unit configurations and process operating parameters. It is therefore an essential step in the design and optimization of a process. Modeling and simulation have been the center of interest of many researchers and various studies have been reported regarding the mathematical representation of biomass conversion processes. Although very few of them deal with integrated BTL processes like the one described in this work, there is a plethora of studies that aim to the understanding and the optimal design of each processing step.

4.1. Gasification modeling

Regarding the modeling and simulation of gasification processes, two alternative perspectives are used in the literature: the particle and the reactor approach. Using the first, a comprehensive model can be constructed accounting for all the phenomena occurring during the gasification of a single biomass particle. That includes the intra-particle transport, physical and chemical phenomena as well as the external interactions of the particle with the reactor walls, bed material, fluidizing gas, etc. The latter approach combines all the thermodynamic and hydrodynamic relations, as well as the reaction chemistry and kinetics in order to simulate and predict the behavior of the whole reactor.

Another distinction between the modeling approaches found in the open literature is the degree of detail that they encompass. The thermodynamic equilibrium approach, also known as the zero-dimensional (0D) model can be used in order to predict the maximum biomass conversion and gasifier efficiency [65]. The model does not take into consideration the spatial dependency of the variables and the flow fields in the gasifier and can be used as a preliminary tool for process design. Depending on the number of dimensional coordinates used, 1D, 2D and 3D models have been developed. 1D models are the most commonly used [66–69] while 2D models have also been reported [70,71]. 3D models contain much detail providing detailed insight on the flow fields inside the gasifier but the computational effort needed for their solution makes them a harsh choice for preliminary design studies. Industrial uses of 3D gasification models are reported by Ravelli et al. [72].

Gasification models can also be largely different in structure due to the different types of gasifiers available as the gasifier type determines the hydrodynamic equations and the geometry of the model. Di Blassi [73] gives a comprehensive model for the prediction of the behavior of a fixed bed updraft gasifier, validated against experimental data. The model is able to predict the experimental results on a laboratory scale, however the author points out the need for further research for the expansion in industrial gasifiers. Tinaut et al. [66] used a model to evaluate operating parameters such as the biomass particle size and the superficial velocity of the fluidizing medium in a downdraft fixed bed gasifier. In a novel approach, Wang et al. [74] examine biomass gasification in two distinct levels, system and pore level using a model that is able to interpret the various phenomena that occur inside the biomass particles due to the fluctuations in the porosity during the thermal degradation of the feedstock.

As the operation of a typical gasifier can be summarized in four steps as described in Section 2.1, an equivalent amount of distinct modeling steps can be used in order to describe its behavior. Jaojaruek and Kumar [75] provide a model for the pyrolysis region of a fixed bed gasifier presenting a more detailed thermal and kinetic analysis of that particular zone, while Gao and Li [67] considered gasification as an integrated process and used a model consisting of two sub-models to simulate the combined contribution of the pyrolysis and reduction zones of the gasifier.

The nature and operation of fluidized bed gasifiers render them a more difficult case for mathematical modeling and simulation as

the hydrodynamics of fluidization and the various phase regimes that are present stiffen the representation and subsequent solution of the problem. Gomez-Barea and Leckner [76] provide a review on fluidized bed gasifiers addressing issues such as vessel types, process kinetics, simulation approaches and many more, while Nemtsov and Zabaniotou [77] present a detailed review of the mathematical modeling of a bubbling fluidized bed reactor.

Radmanesh et al. [68] used a model for the gasification of biomass in a bubbling fluidized bed gasifier. Their model is validated against experimental data, exhibiting a good match. Nikoo and Mahinpey [78] present a modeling and simulation study of an atmospheric fluidized bed gasifier using AspenPlus®. Their study includes the model validation against lab scale experimental results and parametric studies to determine the influence of various operating parameters on the distribution of the final products. Pengmei et al. [79] provide a model for the description of biomass fluidized bed air-steam gasification taking into consideration the reaction kinetics, gas dispersion and assuming instant devolatilization of the sample upon entering the reactor. Ratnadhariya and Channiwala [80] split the gasifier into three distinct zones according to their operation (drying and pyrolysis, oxidation and reduction) and used separate models for each. The interconnections between the gasifier zones were transformed into proper boundary conditions for each of the models and so, a complete mathematical description of the gasifier was achieved.

Corella and Sanz [81] give a pseudo-rigorous model for the simulation of a circulating fluidized bed gasifier. Their model combines mass and heat balances as well as some hydrodynamic considerations and assumptions. An extension of the equilibrium model was adopted by Li et al. [24] to account for the equilibrium deviations of a pilot-scale circulating fluidized bed gasifier. The modified model was able to predict satisfactorily the experimental data.

Watanabe and Otaka [82] developed a model in order to evaluate the performance of an entrained flow gasifier. Their work is a lumped approach consisting of three distinct models accounting for pyrolysis, char combustion and gas phase reactions respectively which enabled them to examine the influence of operating parameters on the process through parametric analyses. Lastly, Yu et al. [83] used a model to predict the hydrogen production from an entrained flow gasifier. Their model emphasizes on the heterogeneous gas–solid reactions which are described by the multi-species of solid phase method as well as the water-gas shift reaction through which the largest quantity of hydrogen is produced.

For the rigorous solution of the models developed in the literature, different computational tools have been used during the numerical simulation. These vary from commercial process model simulators to self-developed programming codes. The contribution of computational fluid dynamics (CFD) for the accurate representation of the phenomena that occur during gasification is also important [72,83,84]. CFD modeling considers the interactions between the liquids and gases in the process by solving the Navier–Stokes equations in conjunction with the classic heat and mass conservation equations. By utilizing CFD modeling, the development of 2D or 3D models is possible and detailed representations of the flow fields can be obtained.

4.2. Steam reforming

The modeling and simulation of single step steam reforming of tar is often considered in the overall gasification model [66,67,76,81,83,85] by implementing the reforming reactions in the overall reaction scheme. On the other hand, when the secondary steam reforming after the gasification step is studied for the production of additional synthesis gas and/or hydrogen, different modeling considerations have to be taken into account as in that case steam reforming represents a separate process.

The modeling of steam reforming processes has been studied broadly. Although most studies focus on the reforming of methane (natural gas), the process can be expanded for a range of volatile hydrocarbons like tar. Regardless of the designated target (hydrogen rich or not) detailed kinetics have to be used if an accurate and reliable model is sought. De Groote and Froment [86] present a model for the steam reforming of methane in a fixed bed reactor over a nickel catalyst, investigating the influence of the feed stream composition on the products. Halabi et al. [87] analyzed a fixed bed reactor for the autothermal steam reforming of methane. They used a 1D model that accounts for the thermochemical and transport phenomena inside the reactor and the simulations show the steady state and dynamic profiles of the reactor with respect to the process operating parameters. Tubular reactors have also been simulated using various models [88–90] for the mathematical description of steam reforming. Xiu et al. [91] proposed a model for the description of a steam reforming process with simultaneous CO_2 capture using catalysts for adsorption. The model includes a fixed bed column reactor packed with an adsorbent for the selective removal of CO_2, taking into account all the intra-particle diffusion phenomena and limitations.

When the maximization of hydrogen production is sought, membrane reactors pose a lucrative alternative to the conventional fixed and fluidized bed reactors. This particular reactor type offers the advantage of selective hydrogen removal through the permeable membrane. This in turn, drives the chemical equilibrium of the reactions to the right and thus the production of hydrogen is enforced. A comparison between the efficiency of a membrane reactor with a conventional fixed bed reactor is reported by Fernandes and Soares [92], while a simulation study for the numerical evaluation of a thermally coupled membrane reactor is presented by Patel and Sunol [93]. Ye et al. [39] studied the influence of the process operating parameters in a membrane reactor using the AspenPlus® process model simulator coupled with a sub-model for the description of the membrane permeation. Finally, Chen and Elnashaie [94] investigated the optimization of reactor configuration and optimal parameter determination for the steam reforming of higher hydrocarbons in a fluidized bed membrane reactor for the production of hydrogen.

4.3. Fischer–Tropsch's synthesis

The simulation of the synthesis of liquid long chain hydrocarbons via the Fischer–Tropsch method relies on the accurate description of the prevailing phenomena inside the reactor vessel. Once again, the reactor configuration plays a major role on the development of the mathematical model. As slurry bubble column reactors exhibit the best efficiency, a lot of modeling and simulation studies have been driven towards the description of these reactors. However, the simulation of this reactor type proves to be rather complex as the mathematical model is comprised of a large system of differential and algebraic equations (DAEs) and usually the bottleneck for these problems is the non-linearity of the system of algebraic equations which is often linked with simulation failures. During the Fischer–Tropsch synthesis reactions in slurry bubble column reactors three phases are present. This fact, when added to the already complex diffusive and convective interactions between the phases creates a formidable problem that needs to be solved.

Troshko and Zdravitch [95] present a CFD modeling study for the accurate description and the quantitative evaluation of the performance of a slurry bubble column reactor. Their model involves a Eulerian multifluid formulation and utilizes the population balance model for the prediction of the bubble distribution

inside the reactor. Schweitzer and Viguie [96] also developed a model for the simulation of a slurry bubble column reactor. The results of their model where compared with experimental ones obtained from lab scale tests; good agreement was observed regarding the distribution of the products. Kim et al. [51] developed a model aiming to the optimization of a slurry bubble column reactor. The process simulation was performed with the help of AspenPlus® simulation software. The ASF equation was used for the prediction of the product distribution and the optimal operating temperature was determined through process optimization. Fernendes [53] and Fernandes and Sousa [97] also present optimization schemes in order to determine the optimal operating conditions of a slurry reactor during Fischer–Tropsch's synthesis, by the means of maximizing certain hydrocarbon products. Their studies include sensitivity analyses for the determination of the influence of operating parameters on the distribution of the final products as well as an optimization algorithm for the identification of the best solution for the problem.

Lozano-Blanco et al. [98] used a combination of a 1D model accounting for two bubble classes and three phases and a single-event micro-kinetics model to study the performance of an industrial bubble column reactor. Single-event micro-kinetics methodology enables the reduction of the model parameters by using the reaction families concept. This results to the formulation of net formation rates for each chemical species that are computed as functions of the individual elementary steps that involve these species.

Jess and Kern [99] developed a model for a multi-tubular fixed bed reactor for Fischer–Tropsch's synthesis. In their work they presented a comparison between a 1D and a 2D model as well as two commercial catalysts, cobalt and iron. According to the authors, the reactor temperature is different for each catalyst and 2D model is, as expected, more accurate and should be used if the necessary data are available. Wang et al. [52] used a 1D model to describe the operation of a fixed bed reactor. Their work contains several simulations in order to determine the influence of operating parameters, such as temperature and pressure on the final product distribution.

Lastly, Pellegrini et al. [59] describe a model for the hydrocracking of the Fischer–Tropsch waxes by using a lumped model, taking into account pseudo-components to tackle the large number of paraffin species involved.

4.4. Integrated systems for thermochemical biomass conversion

The integration of multiple processes into a single flowsheet is an ambitious effort of understanding the structure and the potential interactions of a complicated conversion system. In terms of mathematical modelling and simulation the implications of process integration are often translated as an upright increase of the model complexity caused by the interactions of the various processes. This creates large sets of coupled differential and algebraic equations that inhibit the direct problem solution. The non-linearity that is induced in the system through certain process parameters such the reaction kinetics further impedes the straightforward solution. It is evident that when the optimal solution of a complex thermochemical conversion system such as the one described in Section 3.2, the computational time and effort needed to achieve that increases as well. In order to handle large optimization problems, mixed integer non-linear programming (MINLP) methods can be used [100].

Although much work has been done over the years in the field of process design, modelling and optimization of thermochemical conversion processes, very few studies deal with integrated approaches and even fewer handle biomass conversion to second generation biofuels. Most works focus on the intensification of a single process or the integration between two of the processes mentioned in this work. A common example found in the literature is the integrated gasification combined cycle which is described in Section 3.1.

Emun et al. [14] and Madzivhandila et al. [101] focused on the evaluation and optimization of an integrated gasification combined cycle (IGCC) for power generation. Ng et al. [102] compare two IGCC configurations, one with a subsequent carbon capture and storage step and another without it. Through the rigorous optimization of the integrated processes, the authors concluded that carbon capture and storage ensures better profitability of the process.

Hamelinck et al. [64] and Tijmensen et al. [103] studied the feasibility and economics of integrated biofuels production through the thermochemical conversion of biomass. In their works they evaluate the possible biomass to Fischer–Tropsch's liquid biofuels conversion and electricity generation with the help of AspenPlus® process model simulator. The model used in both works is a dynamic approach of the process which enables the quantitative evaluation of the parameters affecting the process operation. Sudiro and Bertucco [85] developed a hybrid model for the production of Fischer–Tropsch's synthetic liquid biofuels. Through their model, natural gas or coal undergoes steam reforming and subsequent Fischer–Tropsch's synthesis. The model has been simulated in AspenPlus® and integration possibilities including exploitation of recycle streams and heat pinch analysis are analyzed to provide the optimal flowsheet configuration.

In order to achieve a profitable integrated system simple process combinations are not always acceptable. One must thoroughly evaluate each integration alternative and enforce a decision-taking procedure for the determination of the optimal process configuration. Walter and Ensinas [12] discuss the potential for integration on a BTL system concerning both energy and liquid biofuels co-production via gasification combined cycles and conjunction with Fischer–Tropsch's synthesis. Finally, Gassner and Marechal [100] provide a methodology for the integrated optimization of thermochemical energy production from biomass. Their method includes the thermodynamic modelling and optimization of biomass conversion processes combined with heat integration techniques for the design of the most cost-effective process flow diagram.

5. Conclusions

Second generation biofuels derived from lignocellulosic feedstocks are a promising, environmental friendly alternative energy source that currently draws considerable attention. Second generation biofuel technologies are becoming increasingly popular with time even though still in technological investigation regarding the optimization of process design, production routes and product yields.

The thermochemical transformation of biomass into liquid biofuels is a conversion route that relies in the combination of well-established technologies such as gasification and subsequent Fischer–Tropsch's synthesis. This is an important fact that facilitates the transition from current technologies to new ones.

The conjunction of multiple processes creates a lucrative new process for biofuels production but at the same time a rather difficult system for process design studies; the latter stems from the existence of the multiple interactions between the processing steps, each affecting the overall process. This implies the need for strenuous design studies in order to determine the optimal operating conditions for the system.

The optimal design of such systems can be achieved with the help of process integration and optimization tools, which allow the thorough evaluation of different process configuration alternatives

and the simultaneous exploitation of the interactions between the processes in order to establish the optimal solution in terms of production and economic viability.

Although numerous studies deal with the design of each of these processes separately or even with combinations for the co-production of fuels and energy, very few address the thermo-chemical production pathway as a whole. This leads to a lack of literature on the integrated approach of the thermochemical conversion of biomass to biofuels. Aside from summarizing the existing literature on the design and applications of each individual process, this work has shed some light on this, presenting some of the process alternatives as well as the opportunities and bottlenecks for wise valorisation of the interactions between the processing steps of the biomass thermochemical conversion route.

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